1.4690. *Anal.* Calcd. for $C_{11}H_{19}NO_3$: C, 61.97; H, 8.92; N, 6.57. Found: C, 61.51; H, 9.02; N, 6.67.

The isopropyl ester was obtained in 63.3% yield by a conventional esterification using sulfuric acid catalyst, b. p. 155° (2.5 mm.); $n^{25}D$ 1.4619. *Anal.* Calcd. for $C_{13}H_{23}NO_3$: C, 64.73; H, 9.54; N, 5.81; sapn. eq., 241. Found: C, 64.49; H, 9.79; N, 5.83; sapn. eq., 241.8.

1-Phenyl-5-oxo-2-pyrrolidineacetic Acid.—One hundred eighty grams of β-hydromuconic acid (1.25 moles) and 116 g. (1.26 moles) of distilled aniline were heated together in a glass-lined autoclave for three hours at 225°. There was obtained 285 g. of dark viscous sirup which was dried by azeotropic distillation with 200 ml. of absolute ethanol and 400 ml. of benzene. The dried solution deposited dark crystals which were filtered, wt. 93.5 g. The filtrate was concentrated on the steam-bath to a thick sirup which partially crystallized on cooling. The dark crystals so obtained were filtered to give 113.5 g. of crude material, thus bringing the total weight to 207 g. There was obtained 55.6 g. (19.7% yield) of 1-phenyl-5-oxo-2-pyrrolidineacetic acid after recrystallizing several times from water, m. p. 135–136°. *Anal.* Calcd. for $C_{12}H_{13}NO_3$: C, 65.76; H, 5.94; N, 6.39; neut. eq., 219. Found: C, 65.53; H, 5.99; N, 6.29; neut. eq., 215.6.

5-Oxo-2-pyrrolidineacetamide.—This compound, previously reported by Leuchs and Möbis,[2] was prepared by heating 232 g. of diammonium β-hydromuconate at 215° in a stainless steel Parr bomb for three hours. The crude product weighing 159 g. was purified by repeated crystallization from ethyl acetate. There was obtained 108 g. (59.5% yield) of pure amide, m. p. 147–148°. *Anal.* Calcd. for $C_6H_{10}N_2O_2$: C, 50.70; H, 7.04; N, 19.72. Found: C, 50.56; H, 7.03; N, 19.68.

N-1-Dibutyl-5-oxo-2-pyrrolidineacetamide.—Forty-eight grams of bis-(butylammonium) β-hydromuconate, prepared by adding two moles of butylamine to one mole of β-hydromuconic acid in absolute ethanol, was heated in a sealed tube for three hours at 210–215°. The water-white product thus obtained was dissolved in methanol, dried over anhydrous magnesium sulfate and distilled to give an essentially quantitative yield of the substituted pyrrolidone, b. p. 210–212° (2 mm.). *Anal.* Calcd. for $C_{14}H_{26}N_2O_2$: C, 66.14; H, 10.24; N, 11.02. Found: C, 65.38; H, 10.25; N, 11.31.

The corresponding linear diamide, N,N′-dibutyl-β-hydromuconamide of the same empirical formula, was prepared by the action of butylamine on the acid chloride of β-hydromuconic acid. It was a solid, m. p. 167–168°. *Anal.* Found: C, 66.38; H, 10.25; N, 10.62.

The substituted pyrrolidone was hydrolyzed with 6 *N* hydrochloric acid to give a 73% yield of 1-butyl-5-oxo-2-pyrrolidineacetic acid, m. p. 70.5–72.5°. *Anal.* Calcd. for $C_{10}H_{17}NO_3$: C, 60.30; H, 8.55; N, 7.04. Found: C, 60.57; H, 8.55; N, 7.33.

N,1-Dioctadecyl-5-oxo-2-pyrrolidineacetamide.—Forty-five grams of bis-(octadecylammonium) β-hydromuconate was heated at 225–230° for three hours in a sealed tube to give 38 g. (89% yield) of substituted pyrrolidone, m. p. 71–72.5° after crystallizing from ethanol. *Anal.* Calcd. for $C_{42}H_{82}N_2O_2$: C, 78.02; H, 12.69; N, 4.34. Found: C, 78.02; H, 12.71; N, 4.85.

N,1-Diphenyl-5-oxo-2-pyrrolidineacetamide.—A mixture of 33.8 g. of aniline (0.364 mole) and 26.2 g. of β-hydromuconic acid (0.182 mole) was heated in a sealed tube at 110° for twenty minutes. The temperature was raised to 210° and held for one hour. The product, obtained in essentially quantitative yield, was insoluble in benzene and ether and only slightly soluble in ethanol or dioxane. A small sample was crystallized from ethanol, m. p. 245° (dec.). *Anal.* Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.47; H, 6.13; N, 9.52. Found: C, 73.10; H, 6.31; N, 9.94.

N,1-Bis-(*p*-chlorophenyl)-5-oxo-2-pyrrolidineacetamide.—A mixture of 43.6 g. (0.302 mole) of β-hydromuconic acid and 77.1 g. (0.605 mole) of recrystallized *p*-chloroaniline was heated for one hour at 200° in a glass-lined autoclave. The resulting viscous red-colored product was dissolved in 150 ml. of methanol and to the solution (cold) was added 25 ml. of water. The crystals which separated (69.1 g.) were dissolved in methanol, treated with Darco (activated charcoal) and further recrystallized to give 52.1 g. (47.4% yield). A sample of this material was further recrystallized from aqueous methanol to give an analytical sample, m. p. 166.0–166.9°. *Anal.* Calcd. for $C_{18}H_{16}Cl_2N_2O_2$: Cl, 19.56; N, 7.71. Found: Cl, 19.09; N, 7.82.

N,1-Bis-(4-diethylaminocyclohexyl)-5-oxo-2-pyrrolidineacetamide.—The salt formed by adding 50 g. of β-hydromuconic acid (0.347 mole) to 118 g. (0.694 mole) of N,N-diethyl-1,4-cyclohexanediamine at 70–85° was heated for one hour at 200° in a glass-lined autoclave. The straw-colored, viscous product was dissolved in an equal volume of acetone and cooled to give 73 g. of crystals. By repeated crystallization, first from aqueous acetone and finally from ethyl acetate, a total of 50.4 g. (33.2% yield) of N,1-bis-(4-diethylaminocyclohexyl)-5-oxo-2-pyrrolidineacetamide was obtained, m. p. 163.5–165° (slight dec.). *Anal.* Calcd. for $C_{26}H_{48}N_4O_2$: C, 69.64; H, 10.71; N, 12.50. Found: C, 68.93; H, 10.84; N, 12.66.

Summary

A convenient and general method for the synthesis of ecgoninic acid and certain related acids and amides from β-hydromuconic acid is described.

WILMINGTON, DELAWARE RECEIVED JANUARY 6, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Steric Effect of Methylene Groups. V

BY RICHARD T. ARNOLD AND PAUL N. CRAIG[1]

In view of the recent successful results obtained in the evaluation of absorption at certain characteristic wave lengths,[2,3] we have applied this elegant method to our current stereochemical studies.

Evidence has been presented[4,5] already which indicates strongly that methylene groups do not exhibit a constant steric effect and that the value in a particular case depends upon the type of structure in which the group is found. Previous work indicated that the magnitude of this steric influence decreases in the order —CH_2— (in CH_3—) > —CH_2— (in a six-membered ring) ≫ —CH_2— (in a five-membered ring).

Our earlier work has now been extended to include compounds II, III, V and VI, and the ultraviolet spectra of these are compared with I. Unfortunately, numerous attempts to prepare compound IV failed.

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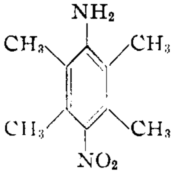
[1] Abstracted from the Ph.D. Thesis of Paul N. Craig; du Pont Fellow 1947–1948.

[2] Remington, THIS JOURNAL, **67**, 1838 (1945).

[3] Brown and Reagan, *ibid.*, **69**, 1032 (1947).

[4] Arnold and Craig, *ibid.*, **70**, 2791 (1948).

[5] Arnold and Richter, *ibid.*, **70**, 3505 (1948).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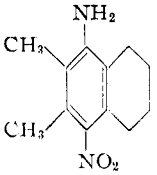
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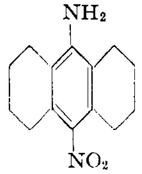
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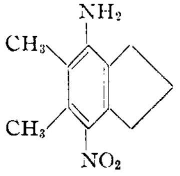
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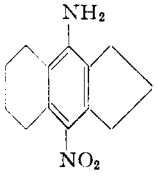
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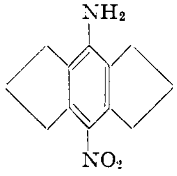

VI

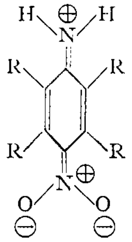
SPECTROPHOTOMETRIC DATA[a]

	λ (max.)	ε × 10^{-3}	λ (ax.)	ε × 10^{-3}
I	395 mμ	1.57	277 mμ	2.5
II	393	1.97	279	2.7
III	397	2.24	270	3.5
V	385	7.3	265	4.8
VI	372	12.8	....	...

[a] Solutions in ethanol (95%) were measured with a Beckman spectrophotometer.

Discussion of Results

Since absorption by *p*-nitroaniline derivatives in the region 375–395 mu. is associated with the planar, dipolar contributing structure VII,[2] it was


VII

anticipated that $\epsilon_{\max.}$ (in this region) would increase steadily in passing through the series I–VI. Such an increase would indicate a gradual lowering in the magnitude of the steric influences about the nitro group which inhibit copolarity between this group and the aromatic ring. Examination of the spectral data shows that this expectation was realized fully and therefore substantiates the conclusion reached in earlier papers of this series.

It is to be noted that for the particular series of compounds reported herein, a given change of structure is accompanied by a rather constant change in the value of $\epsilon_{\max.}$ (375–395 mu.). In particular, replacement of a six-membered ring by a five-membered ring results in an increase (in $\epsilon_{\max.}$) of about 5,000 units. Substitution of two methyl groups by a six-membered ring brings about an average increase of about 330 units. These facts were used to estimate the value of compound VI in advance of its synthesis. It is now believed that compound IV (when prepared) will exhibit a value for $\epsilon_{\max.}$ of approximately 7,000 units (in the region of 385 mu.).

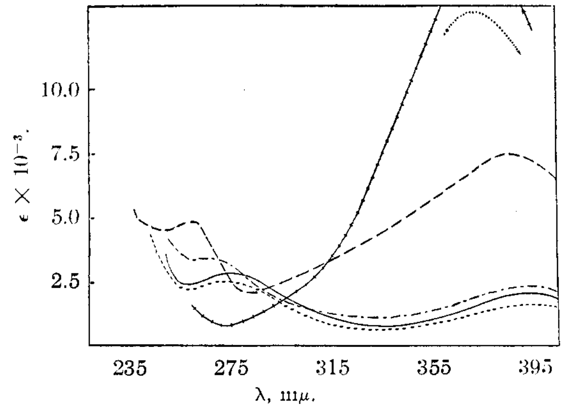
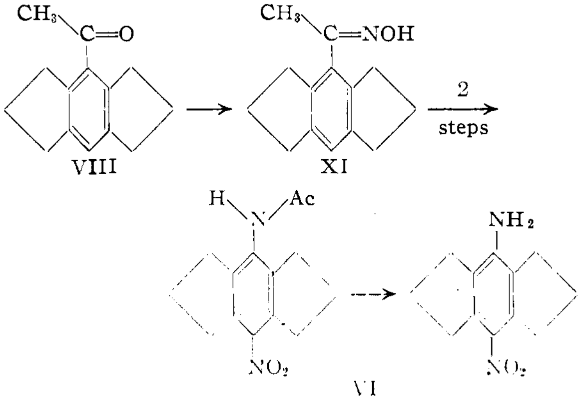


Fig. 1.—Compound I, – – – – –; II, ———; III, — — — — — —; V, — — — — — —; VI, ...; *p*-nitroaniline, + + + +.

Compounds II, III and V were prepared by partial reduction of the corresponding dinitro derivatives. Direct dinitration of the appropriate hydrocarbons required quite different experimental conditions. Indeed, all attempts to dinitrate hydrindacene (from which VI could ultimately be obtained) failed. As a result, compound VI was prepared (as indicated below) by making use of the fact that the carbonyl group of acetohydrindacene (VIII) is not markedly hindered by the methylene groups in the five-membered rings and an oxime (IX) is readily obtained.



Experimental

5,8-Dinitro-6,7-dimethyltetralin.—To a mixture of concentrated sulfuric and nitric acids (10 ml. each) cooled to −40° was added fuming nitric acid (2 ml.) and 6,7-dimethyltetralin (0.6 g.). After being stirred for five minutes, the mixture was poured onto ice with effective stirring. The white product was collected on a filter and recrystallized from ethanol (95%); weight 0.6 g.; m. p. 197°.

Anal. Calcd. for $C_{12}H_{14}O_4N_2$: C, 57.59; H, 5.65. Found: C, 58.03; H, 5.92.

5-Amino-8-nitro-6,7-dimethyltetralin (II).—The above dinitro compound (0.75 g.) dissolved in ethanol (15 ml., 95%) was added to a solution consisting of sodium sulfide monohydrate (0.8 g.), sulfur (0.1 g.) and water (3 ml.). After two hours at the boiling point temperature, the ethanol was distilled out and water (200 ml.) added. Treatment with hot hydrochloric acid (3%) gave a solution which, after filtration, was neutralized with ammonium hydroxide. Recrystallization of the precipitate from ethanol gave the desired product; 0.1 g.; m. p. 129–130°.

Anal. Calcd. for $C_{12}H_{16}O_2N_2$: C, 65.43; H, 7.32. Found: C, 65.15; H, 7.56.

9,10-Dinitro-1,2,3,4,5,6,7,8-octahydroanthracene.—Impure octahydroanthracene (m. p. 72–73°; obtained by the reduction of anthracene with hydrogen and Raney nickel) was dissolved in petroleum ether (b. p. 23–38°) and percolated through a column of alumina and silica gel. Evaporation of the solvent followed by one crystallization from ethanol gave pure octahydroanthracene; m. p. 75–76°.[6]

Pure octahydroanthracene (6.0 g.) was dissolved in chloroform (50 ml.) and to this was added at +10° sulfuric acid (50 ml.). Fuming nitric acid was added dropwise until a tar separated. After being washed with water and sodium bicarbonate solution, the chloroform layer was evaporated to 5 ml. Ethanol (20 ml.) was added and the solution heated to boiling. Needles (3.2 g.) separated from this solution on cooling; m. p. indefinite at 250° (dec.). Recrystallization from a mixture of acetone and ethanol gave needles melting at 295–305° (dec.).[7] The use of octahydroanthracene (m. p. 73–74°) resulted in much lower yields.

Anal. Calcd. for $C_{14}H_{16}O_4N_2$: C, 60.85; H, 5.84. Found: C, 60.70; H, 6.02.

9-Amino-10-nitro-1,2,3,4,5,6,7,8-octahydroanthracene (III).—The above dinitro compound (3.5 g.) was reduced with sodium sulfide solution as described in a previous example; m. p. 205–208° (dec.).

Anal. Calcd. for $C_{14}H_{18}O_2N_2$: C, 68.27; H, 7.37. Found: C, 68.05; H, 7.37.

4,9-Dinitro-5,6,7,8-tetrahydrobenz(f)indane.—A solution of 5,6,7,8-tetrahydrobenz(f)indane (0.6 g., m. p. +4°, $n^{26}D$ 1.5559) and petroleum ether (200 ml., b. p. 28–38°) was swirled for five minutes over an ice-cold mixture of concentrated sulfuric (20 ml.) and nitric (5 ml.) acids. The organic layer was separated and combined with a petroleum ether extract of the acid mixture. After being washed with sodium bicarbonate solution, the petroleum ether layer was evaporated to dryness. Recrystallization from aqueous ethanol gave white needles; yield 100 mg.; m. p. 218–220°.

Anal. Calcd. for $C_{13}H_{14}O_4N_2$: C, 59.55; H, 5.38. Found: C, 59.94; H, 5.62.

This method was the only one of many tried which gave any identifiable product.

4-Amino-9-nitro-5,6,7,8-tetrahydrobenz(f)indane (V).—Reduction of the corresponding dinitro compound (100 mg.) in ethanol (20 ml.) with sodium sulfide monohydrate (1.0 g.) as described above gave yellow needles; yield 50 mg.; m. p. 163°.

Anal. Calcd. for $C_{13}H_{16}O_2N_2$: C, 67.20; H, 6.94. Found: C, 67.09; H, 7.04.

Oxime of 4-Acetohydrindacene (IX).—The ketone (VIII, 4.6 g.) was treated with hydroxylamine hydrochloride (10 g.), sodium hydroxide (80 ml., 7%) and sufficient ethanol to effect solution at steam-bath temperature. After heating for thirty minutes the solution was carefully diluted with water and chilled to precipitate the oxime; 4.0 g.; m. p. 161–163°.

Anal. Calcd. for $C_{14}H_{17}ON$: C, 78.10; H, 7.96. Found: C, 77.85; H, 8.31.

4-Acetamidohydrindacene.—The oxime IX (4 g.) was dissolved in a mixture of acetic acid (30 ml.) and acetic anhydride (30 ml.) and saturated at 0° with dry hydrogen chloride. This mixture was allowed to stand at room temperature for eighteen hours. Dilution with water followed by cooling resulted in white needles; 3.7 g.; m. p. 248–250°.

Anal. Calcd. for $C_{14}H_{17}ON$: C, 78.10; H, 7.96. Found: C, 77.89; H, 7.98.

4-Amino-8-nitrohydrindacene.—Nitration of the above acetamidohydrindacene (1 g.) with fuming nitric acid (10 ml.) and acetic anhydride (30 ml.) at 0–5° gave the desired 4-acetamide-8-nitrohydrindacene; 0.35 g.; m. p. 267–268°.

Anal. Calcd. for $C_{14}H_{16}O_3N_2$: C, 64.62; H, 6.1. Found: C, 63.99; H, 6.24.

This compound (although slightly impure) was hydrolyzed by boiling with sulfuric acid (25 ml., 50%) for one hour. The cooled, filtered solution was cautiously neutralized with sodium hydroxide and the precipitated nitroamine collected on a filter. Recrystallization first from aqueous ethanol and then from benzene–petroleum ether (b. p. 60–68°) gave 70 mg. of the yellow nitroamine; m. p. 230–232°.

Anal. Calcd. for $C_{12}H_{14}O_2N_2$: C, 66.03; H, 6.47. Found: C, 65.96; H, 6.73.

Summary

1. Ultraviolet spectra have been measured for a series of substituted *p*-nitroamines related to hydrindene, tetralin and *o*-xylene.

2. The results indicate that the effective steric hindrance of a methylene group is not constant but depends upon the type of structure in which it is found.

MINNEAPOLIS, MINNESOTA

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(6) Schroeder, *Ber.*, **57**, 1990 (1924), reports 73–74°.

(7) Schroeder, *ibid.*, **60**, 2035 (1927), reports this substance in a footnote as melting at 305–310°.